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Effect of Etched Substrates in Long-Term Stability Testing of Dye-Sensitized Solar Cells

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The dye-sensitized solar cells (DSSCs) examine long-term stability tests were prepared to SnO_2:F (FTO) glass substrates patterned by the etching method were applied to the electrode on the device using polyethyleneglycol (PEG) electrolyte. We investigated the effect of patterned SnO_2:F (FTO) glass substrates on the power conversion efficiency and long-term stability of DSSCs. The patterned devices maintained over 83% of its initial overall power conversion efficiency after 720 hours aging at room temperature, while the devices using non-patterned FTO glass substrates showed drastic decrease in performances.

Keywords: dye-sensitized solar cells; effect of etched substrates; long-term stability test

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are composed of a few micrometer-thick films consisting of a nanocrystalline metal oxide covered with a monolayer of Ru-bipyridyl-based charge-transfer dye, an electrolyte solution containing the iodide/triiodide couple, and a platinum metal electrode. These cells are an interesting and promising alternative to conventional silicon solar cells, and have achieved certified conversion efficiencies of 10.4% and lifetime expectancies of at least 10 years for outdoor use in laboratories [1–5].

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However, the presence of traditional liquid electrolytes in these cells has some problems such as reliability, a less long-term stability, a need for hermetic sealing, and scale up of the manufacturing process have yet to be overcome for commercial production.

The long-term stability of the DSSC system has been subject of concern during the past years of development of technology. Since then long-term stability of the DSSC has been investigated extensively in an EU-project LOTS-DCS in collaboration between ECN Solar Energy, Solaronix SA, and Institut fur Angewandte Photovoltaik INAP [6]. High stability for a Ru-based dye was reported already by ÓRegan and Grätzel together with the presentation of the high efficiencies of the cell. Grätzel and Tributsch on the other hand detected the N3 dye unstable, and also reported number of the difficulties in the long-term stability of the cells, such as sealing problems and decomposition of the electrolyte. Their work focused on the intrinsic chemical stability of the cells, visible light, UV light and temperature were used as stress factor. The degradation of the cells performance, when observed, was assigned to the degradation of the electrolyte instead of to the degradation of the dye [7].

The overall stability of DSSC is controlled by two factors, namely physical and chemical stability. Physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technological problem, for which solutions can be found by using suitable sealing materials and techniques [8–10]. The intrinsic chemical stability is related to irreversible electrochemical and thermal degradation of the dye or electrolyte components, which might ccur during operation of the DSSC. Recently, many long-term stability test have been developed by IEC standard, such as annealing (85°C, 85% RH), humidity (–40 to 85°C), thermal cycling and light soaking. However, internationally accepted ageing tests have not yet been established for organic-based solar cells, such as the liquid-junction DSC, which is understandable considering the stage of development of these cells [11]. In fact, these cells sealed with polymer hot melts, filled with volatile solvents like acetonitrile show evaporation of the electrolyte with thermal annealing at 85°C because of its thermal stress. In addition, this test is very hard to compare results from different laboratories, because of different testing conditions, such as various electrolyte combinations, containing different dye, sealing method, sealing materials, and TiO_2. Therefore, ageing test results should be considered as laboratory specific or not valid in general.

In this study, four different kinds of the DSSCs were fabricated to long-term stability tests and theirs photovoltaic performance

stabilities were measured by using a Solar Simulator. In addition, on these devices using the polymer electrolyte, the nanopore-filled electrolytes into the nanocrystalline TiO_2 layer were investigated by using Scanning Electron Microscope (SEM) after the long-term stability test.

2. EXPERIMENTAL

2.1. Materials

TiO_2 paste such as Ti-Nanoxide HT/SP (Colloidal anatase particle size: ~ 9 nm), cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) dye (N3 dye), 1-propyl-3-methylimidazolium iodide (PMImI) as an ionic liquid, Amosil 4 as a sealing material, FTO glass (15 Ω/square) and Pt paste (Pt catalyst T/SP) were purchased from Solaronix SA. Iodine (I_2), propylene carbonate (PC), ethylene carbonate (EC), and tetrabutylammonium iodide (TBAI) were purchased from Aldrich Co. and used without the purification. Polyethyleneglycol (PEG, $M_w = 20{,}000$) was purchased from Fluka Co.

2.2. Fabrications of DSSC Devices to Long-Term Stability Tests

As a substrate, the FTO glass substrates were patterned with zinc powder and hydrogen chloride (HCl) to form the required electrode pattern [12]. After that, the working electrode was prepared as follows. Thickness of $10 \sim 15\,\mu$m of the TiO_2 paste was spreaded on FTO glass by the doctor blade method, followed by sintering at 120°C for approximately 30 min and at 500°C for about 30 min. The sintering process was completed and the TiO_2 deposited electrode was cooled down from 500°C to *ca*. 60°C at the controlled cooling rate (5°C/min) to avoid any cracking of the glass. The nanostructured TiO_2 electrode was dipped in a concentration of 10 mg of N3 dye per 50 ml of an absolute ethanol solution at room temperature over night. The TiO_2 electrode adsorbed dyes were dipped in the electrolyte solution at room temperature for 24 hours. The PEG electrolyte solution was prepared as previously reported [13,14]. The electrolyte was casted onto the TiO_2 electrode adsorbed dyes and was then dried at about 60°C for 2 hours to evaporate wholly the solvent. The counter electrode was also prepared by a similar method to that which the TiO_2 film was coated. Pt paste was placed on an FTO glass by sintering to at 100°C for approximately 30 min prior to firing at 400°C for 30 min. In assembling of DSSC devices, the working electrode and the counter electrode were clamped together.

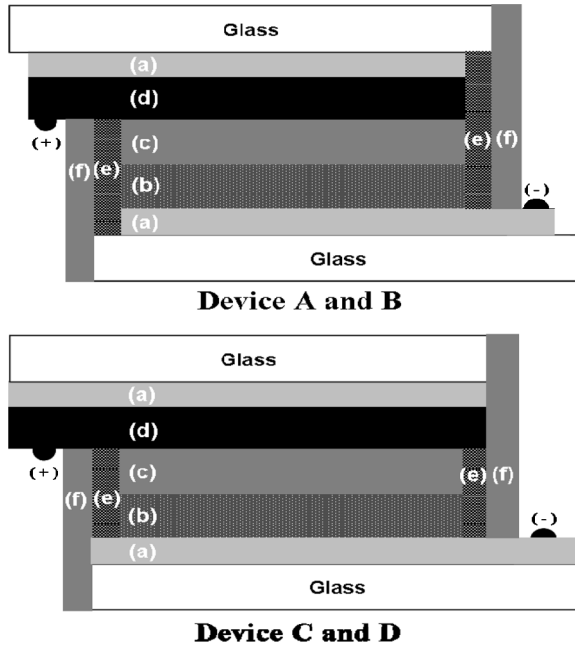

FIGURE 1 The cross-section structure of the DSSC devices to long-term stability tests (Original FTO glass width: 20 mm); Device A and B: (a) patterned FTO (width: 16 mm), (b) TiO_2 with dye (width: 7 mm), (c) Electrolyte (width: 7 mm), (d) Pt (width: 16 mm), (e) Inner sealant, (f) Outer sealant; Device C and D: (a) non-patterned FTO (width: 20 mm), (b), (c) same as upper, (d) Pt (width: 20 mm), (e), (f) same as upper.

The edges of the devices were sealed with Amosil 4 to protect the corrosion during the long-term stability test, DSSC devices have been stored in dark and air at room temperature. The structure of the fabricated DSSC device is shown in Figure 1. The device A and B were fabricated using patterned FTO glass substrates as described above, and the device C and D were fabricated using the non-patterned FTO glass substrates to compare with the effect of patterned substrates on photovoltaic performances in long-term stability.

2.3. Measurements

The nanostructure and surface morphology of the nanostructured TiO_2 films were characterized by Scanning Electron Microscope (SEM). The sheet resistances of the several substrates were measured by using Low Resistivity-Meter (MCP-T610). The photovoltaic

characteristics of DSSC devices were measured using a Solar Simulator (150 W simulator, PEC-L11, PECCELL) under a simulated solar light with an ARC Lamp power supply (AM 1.5, 100 mW/cm^2). The solar simulator was calibrated to Si reference cell verified. The active area of DSSC device measured by using a black mask was 0.49 cm^2 [15].

3. RESULTS AND DISCUSSION

Effective FTO glass substrates in DSSC should have high electrical conductivity combined with low absorption of the visible light. However, the decrease of the resistivity is correlated with a decreased transmission for a given material. In particular for device used without compact TiO_2 layer, the interfacial and material-compatibility properties of the FTO glass substrates are also important, determining the attachment of the deposited material to the FTO glass substrates. Therefore, we measured sheet resistances of FTO glass substrates for long-term stability tests using the four-point technique [16,17], and the results of FTO glass substrates resistance tests are summarized in Table 1. It can be seen that the FTO glass substrates after sintering at 500°C increased the sheet resistance only 2–5%, and the patterned FTO glass substrates after etching process a little increased the sheet resistance from 12.72 Ω to 16.28 Ω. Also, the TiO_2 films deposited on FTO glass substrate with thickness of 12 um increased the sheet resistance about 2–6%. It is that the TiO_2 films increased the sheet resistance of the glaze, and expected that the sheet resistance of the patterned FTO glass substrate is not affected on the overall performance of DSSC devices even if it were deposited TiO_2 layer after sintering process at 500°C.

To investigate the effect of the patterned FTO glass substrates on long-term stability tests, we fabricated the four types of DSSC devices

TABLE 1 The Sheet Resistances of FTO Glass Substrates used for the Preparation of Long-Term Stability Tests

Glass type	R_0[1] (Ω/□)	R_1[2] (Ω/□)	R_2[3] (Ω/□)
Non-patterned FTO substrates	12.72	13.31	14.14
Patterned FTO substrates	16.28	16.60	16.92

[1]Initial sheet resistance.
[2]Sheet resistance after sintering at a temperature of 500°C.
[3]Sheet resistance of the TiO_2 films deposited on FTO substrate (after sintering at a temperature of 500°C).

TABLE 2 The Photovoltaic Performances and Maintenance Rates After 720 hours Aging of Device A, B, C, and D Under Light Density: 100 mW/cm^2; AM 1.5, Active Area: 0.49 cm^2

	V_{oc}[1] (V)			J_{sc}[2](mA/cm^2)			Fill Factor			Efficiency (%)		
Device	I[3]	F[4]	M.R[5] (%)	I	F	M.R (%)	I	F	M.R (%)	I	F	M.R (%)
Device A[6]	0.72	0.72	100	6.59	6.31	95.8	0.60	0.52	86.7	2.84	2.38	83.8
Device B[7]	0.71	0.66	93.0	5.67	5.06	89.2	0.62	0.60	96.8	2.51	1.99	79.3
Device C[8]	0.73	0.69	94.5	6.74	1.43	78.0	0.62	0.28	45.2	3.03	0.27	9.0
Device D[9]	0.71	0.65	91.5	5.65	4.89	86.5	0.62	0.61	98.4	2.50	1.92	76.8

[1]Open-circuit voltage.
[2]Short-circuit current density.
[3]Initial value.
[4]Value measured after 720 hours.
[5]Maintenance rate after 720 hours.
[6]Used patterned FTO glass substrates; only inner sealant not out sealant.
[7]Used patterned FTO glass substrates; both inner sealant and out sealant.
[8]Used non-patterned FTO glass substrates; only inner sealant not out sealant.
[9]Used non-patterned FTO glass substrates; both inner sealant and out sealant.

and theirs photovoltaic performances on the function of time were measured by the Solar Simulator. The initial-/after 720 hours- photovoltaic characteristics and the maintenance rate of the DSSC devices are summarized in Table 2. After 720 hours aging, the power conversion efficiencies of the device A and B using the patterned FTO glass substrates showed 1.99–2.38%, and the power conversion efficiencies of the device C and D using non-patterned FTO glass substrates were 0.27–1.92%.

Figure 2 shows that the device A maintained over 83% of its initial the overall power conversion efficiency after 720 hours aging at room temperature in air, while the device C and D using non-patterned FTO glass substrates showed drastic decrease in performances. In particular, for the open-circuit voltage (V_{oc}), no change was observed after 720 h aging, and the short-circuit current density (J_{sc}) of 6.31 mA/cm^2 was slightly lower than its initial value of 6.59 mA/cm^2. From this result, it was found that the condition of the patterned FTO substrate is more proper on long-term stability tests.

To confirm nanopore-filled PEG electrolytes into TiO_2 layer after long-term, the surface and the cross-section images of the DSSC devices after 2 hours and 720 hours were investigated by SEM. As shown in Figures 3(B) and (C), the small grains with dense structures and well PEG-covered surface have been observed, and it was found

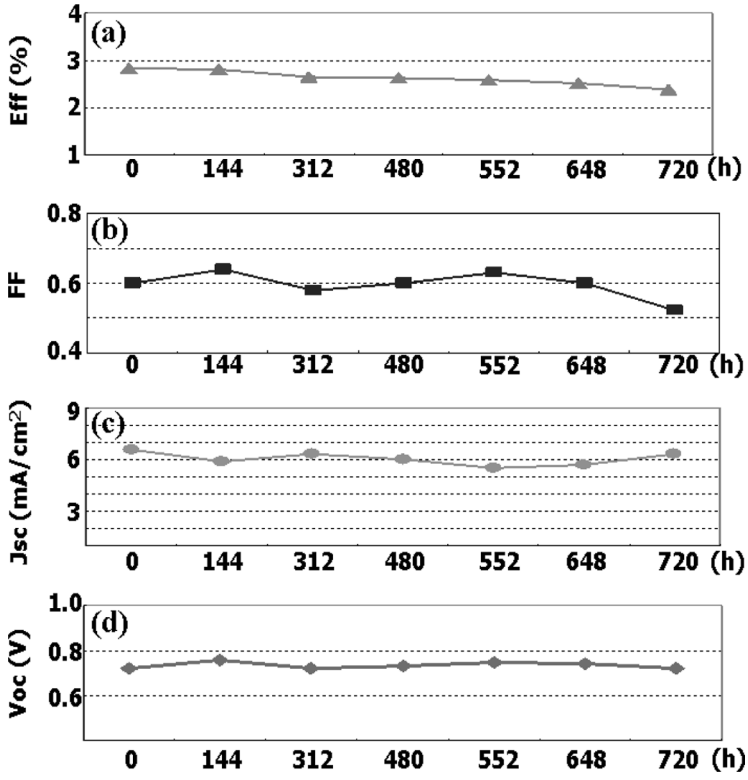

FIGURE 2 Temporal evolution of photovoltaic parameters of Device A during stored in the dark and air at room temperature. Efficiency (a); Fill Factor (b); J_{sc} (c); V_{oc} (d).

that the PEG electrolyte was penetrated into the porous TiO_2 film. The thickness of TiO_2 films calculated from the cross-section of TiO_2 films were measured at about 12 um, and the PEG electrolyte-filled TiO_2-films (Figs. 3(b) and 3(c)) show lower contrast and softened features, compared to the nanocrystalline TiO_2 films in Figure 3(a). The PEG electrolyte-filled TiO_2 film after 2 hours drying at 60°C in dry oven show an average grain size significantly larger than the primary TiO_2 particle size visible in the nanocrystalline TiO_2 films, indicating homogeneous and effective pore filling. The PEG electrolyte-filled TiO_2 film after 720 hours aging at room temperature, however, appear little inhomogeneous, with some areas showing similar contrast to the nanocrystalline TiO_2 films.

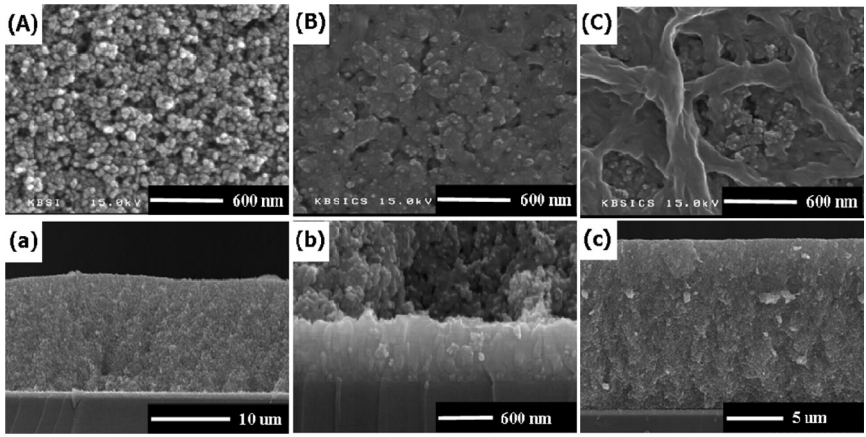

FIGURE 3 The SEM surface images [(A)–(C)], and the cross-section images [(a)–(c)] of the device A. (A) and (a): the nanocrystalline TiO_2 films; (B) and (b): the PEG electrolyte-filled TiO_2 film (after 2 hours drying at 60°C in dry oven); (C) and (c): the PEG electrolyte-filled TiO_2 film (after 720 hours aging at room temperature).

4. CONCLUSION

The four different kinds of the DSSC devices for long-term stability tests were successfully fabricated using PEG electrolyte. After 720 hours aging, the power conversion efficiencies of the DSSC devices using the patterned FTO glass substrates showed 1.99–2.38%, and the efficiencies of the DSSC devices using non-patterned FTO glass substrates were 0.27–1.92%. The patterned FTO glass substrates were applied to the electrode of the DSSC devices and the power conversion efficiencies of the DSSC devices sealedusing appropriate sealing materials to protect the corrosion maintained over 83% of its initial the overall power conversion efficiency after 720 hours aging at room temperature. In addition, it was found that the PEG electrolyte was penetrated into the porous TiO_2 film by the SEM.

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